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Sputtered Thin Film Coatings

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30.1 History

Sputtering was discovered in 1852 when Grove observed metal deposits at the cathodes of a cold cathode glow discharge. Until 1908 it was generally believed that the deposits resulted from evaporation at hot spots on the cathodes. However, between 1908 and 1960, experiments with obliquely incident ions and sputtering of single crystals by ion beams tended to support a momentum transfer mechanism rather than evaporation. Sputtering was used to coat mirrors as early as 1887, finding other applications such as coating fabrics and phonograph wax masters in the 1920s and 1930s. The subsequent important process improvements of radio frequency (rf) sputtering, allowing the direct deposition of insulators, and magnetron sputtering, which enables much higher deposition rates with less substrate damage, have evolved more recently. These two developments have allowed sputtering to compete effectively with other physical vapor deposition processes such as electron beam and thermal evaporation for the deposition of high quality metal, alloy, and simple organic compound coatings, and to establish its position as one of the more important thin film deposition techniques.

30.2 General Principles of Sputtering

Sputtering is a momentum transfer process. When a particle strikes a surface, the processes that follows impact depend on the energy of the incident particle, the angle of incidence, the binding energy of surface atoms, and the mass of the colliding particles ([Figure 30.1](#)).

In sputtering, the incident particles are usually ions, because they can be accelerated by an applied electrical potential. If the kinetic energy with which they strike the surface is less than about 5 eV, they

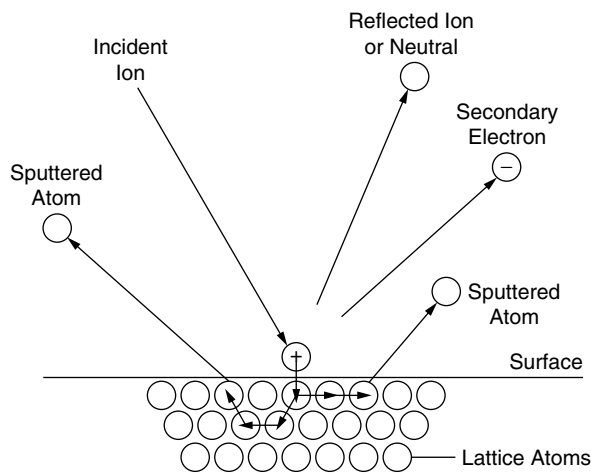


FIGURE 30.1 Schematic representation of some of the processes that follow ion impact during sputtering. (Courtesy of W. H. Brady Co.)

will likely be reflected or absorbed on the surface. When the kinetic energy exceeds the surface atom binding energy, surface damage will occur as atoms are forced into new lattice positions. At incident ion kinetic energies above a threshold, typically 10 to 30 eV, atoms may be dislodged or sputtered from the surface. At normal incidence, multiple internal collisions are required, but at lower angles, sputtered atoms can be produced directly. These sputtered atoms and ions can be condensed on a substrate to form a thin film coating.

Energetic ion bombardment is usually achieved by a low pressure process of the glow discharge type. The basic process configuration, in this case diode, is shown in Figure 30.2. The vacuum chamber is equipped with a target (cathode), the source of coating material, and a substrate to be coated. To dissipate the considerable heat generated in the target during the sputtering process, it is usually bonded to a water-cooled metal (copper) backing plate with solder or conductive epoxy. The target also may be directly cooled by water for greater cooling capacity. The chamber is evacuated and then backfilled with an inert gas, usually argon, to a pressure of 10^{-3} to 10^{-1} torr.* An electrical potential is applied between the target (cathode) and substrate holder (anode). This produces a low pressure glow discharge

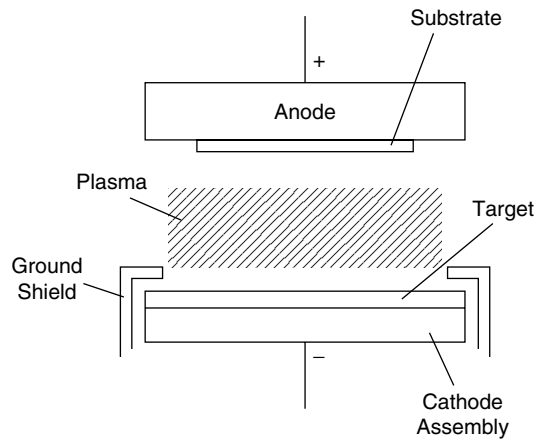


FIGURE 30.2 Schematic representation of a diode sputtering assembly. (Courtesy of W. H. Brady Co.)

*1 Pascal (Pa) = 1 N/m² = 0.075 Torr.

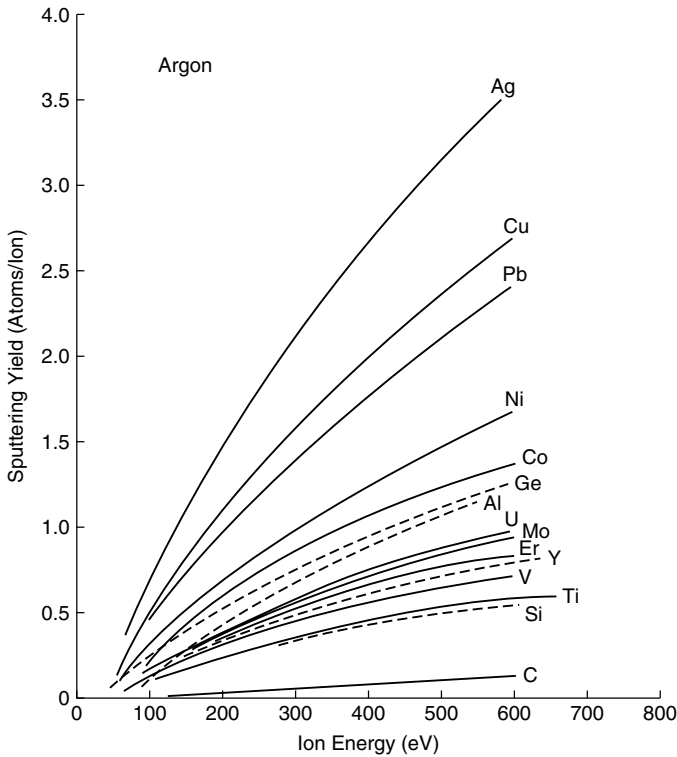


FIGURE 30.3 Variation of sputtering yield with ion energy at normal angle of incidence. (From J. A. Thornton, in *Deposition Technologies for Films and Coatings*, R. K. Bunshah, Ed. Park Ridge NJ: Noyes Publications, 1982, p. 179.)

or plasma between the two electrodes. Grounded dark space shields are used to prevent a discharge from forming in undesirable areas. In a dc glow discharge of this type, current is carried by electrons that are collected from the plasma by an anode and by positive ions leaving the plasma as they are accelerated toward the target. A continuous supply of additional ions and electrons must be available if the discharge is to be sustained. Some of the ions striking the target surface generate secondary electrons, which are accelerated by the cathode potential. These electrons, with energies approaching the applied potential, enter the plasma and ionize gas atoms, producing the necessary additional ions and electrons to sustain the discharge.

The relative rates of deposition for different materials depend largely on the sputter for different materials, the sputter yield (Figure 30.3), defined as the number of target atoms ejected per incident particle. Sputter yield depends on the target material, silver showing the highest yield, and generally increases with incident ion energy and mass.

30.3 Sputter Deposition Sources

30.3.1 Direct Current Diode Sputtering

The simplest and oldest sputter deposition source is dc diode. The two electrodes are usually parallel to each other, spaced 4 to 8 cm apart and the substrate is placed on the anode as in Figure 30.2. The applied potential is typically 1000 to 3000 V dc with argon pressures of about 0.075 to 0.12 torr. The dc diode configuration has important disadvantages, including low deposition rate ($\sim 400 \text{ \AA/min}$ for metals), high working gas pressure, targets limited to electrical conductors, and bombardment of the substrate by plasma electrons, resulting in substrate heating. The cathode systems discussed next can be used to improve on the performance of the dc diode.

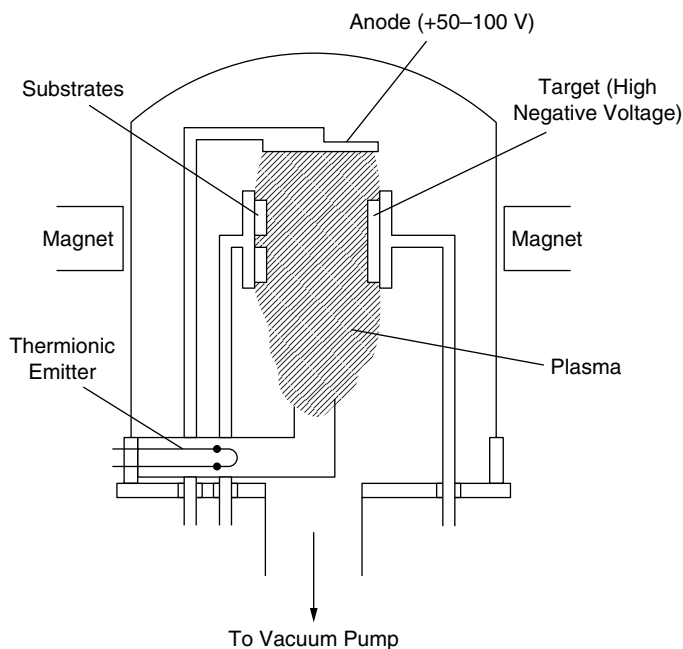


FIGURE 30.4 Schematic representation of a triode sputtering process. (Courtesy of W. H. Brady Co.)

30.3.2 Triode Sputtering

A heated filament (Figure 30.4) is used as a secondary source of electrons for the discharge; an external magnet can also be used to confine electrons and increase isolation probability. Triodes can produce much higher deposition rates, up to several thousand angstroms per minute, at lower pressures (0.5 to 1×10^{-3} torr) and voltages (50 to 100 V). The usefulness of triodes has been limited by difficulties in scaling up to large cathode sizes and corrosion of the emitter filament by chamber gases.

30.3.3 Radio Frequency Sputtering

Nonconducting materials cannot be directly sputtered with an applied dc voltage because of positive charge accumulation on the target surface. If an ac potential of sufficiently high frequency is applied, an effective negative bias voltage is produced such that the number of electrons that arrive at the target while it is positive equals the number of ions that arrive while it is negative. Because the mass of the electron is very small relative to ions present, the target is positive for only a very short time, and deposition rates for rf diode are almost equivalent to dc diode. This resulting negative bias allows sputtering of an insulating target. The frequency used in most practical applications is usually 13.56 MHz, a radio frequency band allocated for industrial purposes by the Federal Communications Commission. Rf sputtering allows insulators as well as conductors and semiconductors to be deposited with the same equipment and also permits sputtering at a lower pressure (5 to 15×10^{-3} torr). One major disadvantage of rf sputtering is the need for electromagnetic shielding to block the rf radiation. Also, the power supplies, matching network, and other components necessary to achieve a resonant rf network are very complex.

30.3.4 Magnetron Sputtering

The magnetron cathode is essentially a magnetically enhanced diode. Magnetic fields are used to form an electron trap that, in conjunction with the cathode surface, confines the $E \times B$ (electric field strength $\times$ magnetic flux density) electron drift currents to a closed-loop path on the surface of the target. This

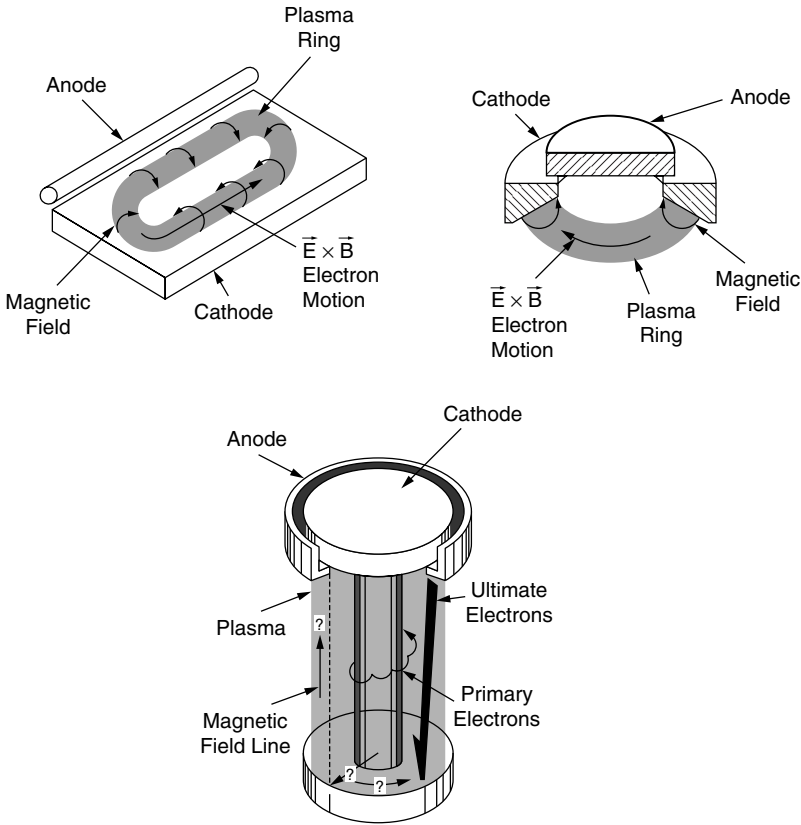


FIGURE 30.5 Clockwise from upper left: schematic representations of planar magnetron, gun-type magnetron, and cylindrical post magnetron sputtering sources. (Adapted from J. A. Thornton, in *Deposition Technologies for Films and Coatings*, R. F. Bunshah, Ed. Park Ridge NJ: Noyes Publications, 1982, pp. 194–195.)

“racetrack” effectively increases the number of ionizing collisions per electron in the plasma. The magnetic confinement near the target results in higher achievable current densities at lower pressures (10^{-3} to 10^{-2} torr), nearly independent of voltage. This manner of cathode operation is described as the magnetron mode and is capable of providing much higher deposition rates (10 times dc diode) with less electron bombardment of the substrate and therefore less heating. Factors affecting deposition rate are power density on the target, erosion area, distance to the substrate, target material, sputter yield, and gas pressure. Dc is usually used for magnetron sputtering, but rf can be used for insulators or semiconductors. When magnetic materials are sputtered, a thinner target is often necessary to maintain sufficient magnetic field strength above the target surface. The three most common magnetron cathode designs, described below, are illustrated in Figure 30.5.

30.3.4.1 Planar Magnetron

An array of permanent magnets is placed behind a flat, circular or rectangular target. The magnets are arranged such that areas in which the magnetic field lines are parallel to the target surface form a closed loop on the surface. Surrounding this loop, the magnetic field lines generally enter the target, perpendicular to its surface. This produces an elongated electron racetrack and erosion pattern on the target surface. Because of the nonuniformity in target erosion, utilization of target material is poor, typically 26 to 45%. This also results in nonuniform deposition on a stationary target. Uniformity is provided by substrate motion, usually linear or planetary, combined with uniformity aperture shielding. Planar magnetron cathodes are usually operated at 300 to 700 V providing a current density of 4 to 60 mA/cm² or a power density of 1 to 36 W/cm².

Deposition rates are generally proportional to the power delivered to the target. Much of this power is dissipated as target heating. The primary factor limiting magnetron deposition rates is the amount of power that can be applied to the target without causing it to melt, crack, or warp. This is controlled by the cathode water cooling design, and the thermal conductivity of the target, the backing plate, and the interface between them. The planar magnetron cathode has been scaled up in production applications to several meters in length and serves as an important industrial coating tool.

30.3.4.2 Cylindrical Magnetron

Two variations on a cylindrical cathode design can be used to coat large surface areas: the cylindrical post magnetron, which sputters outward from a central post target, and the cylindrical hollow or inverted magnetron, which has target erosion on the inner wall of a cylindrical target. Operating parameters are similar to the planar magnetron. The $E \times B$ current closes on itself by going around the post or cylinder. Electrostatic or magnetic containment is often used to minimize end losses. Erosion is uniform along the post or inside of the cylinder. This enables fairly uniform coating without substrate movement. Hollow cathodes are especially effective at coating objects of complex shapes. Another cylindrical cathode, the rotatable magnetron, uses a magnet array similar to a planar magnetron and rotates the target or magnets to obtain uniform erosion.

30.3.4.3 Ring or Gun Magnetron

The ring or gun magnetron source includes a circular cathode and a concentric centrally located anode. As with other magnetrons, high deposition rates are possible with little substrate heating. Because of the circular design, planetary substrate motion is necessary for deposition uniformity. This design is extensively used for small-scale applications but has not been scaled up to larger dimensions. Arrays of these cathodes have been used to coat large areas.

30.3.5 Beam Sputtering

A separate ion beam source (Figure 30.6), as opposed to a glow discharge, may be used to erode the surface of a target. The energy, direction, and current density of the ion beam may be controlled independently, and it is possible to work at background pressures lower than other sputter deposition methods used. Unique film properties can sometimes be obtained using ion beam deposition, but it is generally limited to coverage of rather small areas and lower deposition rates.

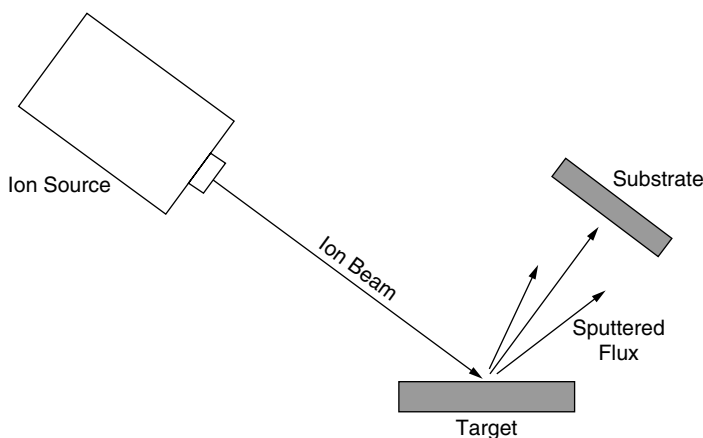


FIGURE 30.6 Schematic representation of ion beam sputtering source showing relative locations of target and substrate. (From J. A. Thornton, in *Deposition Technologies for Films and Coatings*, R. K. Bunshah, Ed. Park Ridge, NJ: Noyes Publications, 1982, p. 211.)

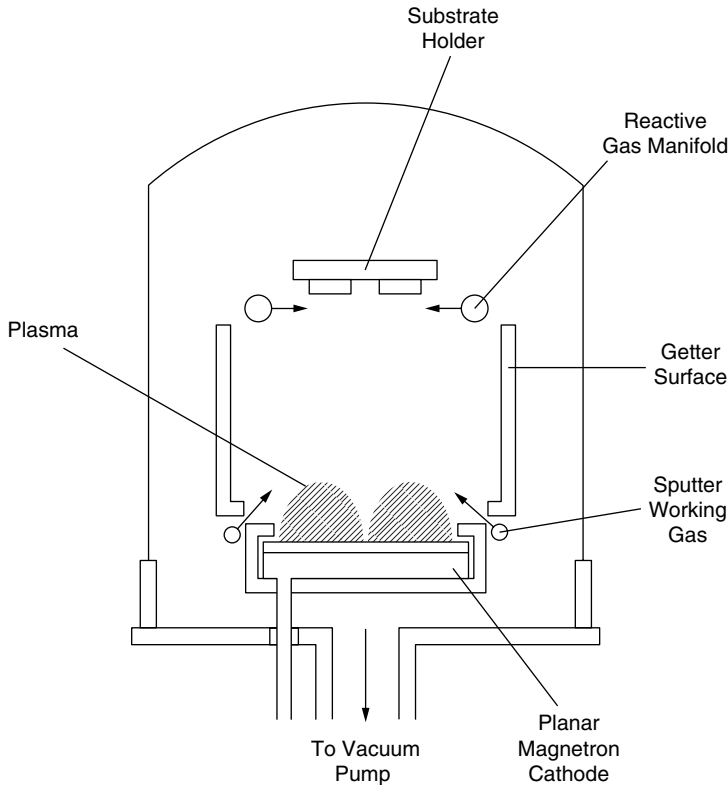


FIGURE 30.7 Schematic representation of a reactive sputtering apparatus. (Courtesy of W. H. Brady Co.)

30.3.6 Reactive Sputtering

Argon is usually employed as the working gas in sputter deposition processes. It is relatively inert, being incorporated in the growing film only when trapped or embedded in its surface. Other more reactive gases such as water vapors, oxygen, and nitrogen are normally present in the deposition chamber as low level contaminants, which have been outgassed from the substrate, target, and chamber walls. These gases may be incorporated into the growing film by reacting with condensed atoms on the substrate surface, forming small amounts of oxides, nitrites, carbides, and other similar compounds of the sputtered material.

In reactive sputtering, gases are intentionally introduced into the deposition chamber to completely react with the forming thin film. A gas manifold system (Figure 30.7) is often used to provide uniform distribution of the reactive gas at the substrate and minimize reactive gas at the target surface.

Reactive sputtering is a very nonlinear process. The growing film on the substrate acts like a getter pump for the reactive gas up to the pressure at which a stoichiometric compound is formed. At this point, the pumping rate of the substrate decreases substantially, and reactive gas pressure increases in the chamber. This gas may react with the surface of the target, resulting in decreased deposition rates due to lower sputter yields of compounds and other factors. Consequently, most reactive deposition processes attempt to work near the transition region of the target, where stoichiometric compounds are formed at the substrate and the cathode target is metallic. Reactive sputtering therefore permits the formation of compounds from simple metallic targets in the dc mode or rf mode. This process is widely used for deposition of oxides and nitrites such as silicon oxides, silicon nitrite, titanium nitride, and indium tin oxide.

30.4 Other Process Considerations

Vacuum chambers used for sputtering have to be capable of producing a vacuum better than 5×10^{-4} torr to minimize contamination from background gases. A load lock is used on some devices when contamination of the sputter chamber by gas absorbed when the chamber is opened is unacceptable, or to decrease pump down time. A wide variety of pumping systems are used including diffusion, turbomolecular, and cryogenic pumps. Throttling of the pumps is necessary in many cases due to high working pressures.

Most target materials have considerable surface contamination accumulated during manufacture and storage. Targets are presputtered to a depth sufficient to remove these contaminants before deposition. A shutter is often used to protect the substrate from the contamination while the target is being cleaned.

The sputtering process can be very dependent on such equipment design factors as gas distribution systems, position of pumps, and distance from target to substrate. These factors and others must be carefully considered when transferring a process from one chamber to another or when scaling up to production levels.

A major factor controlling equipment configuration is the nature of the substrate. The substrate may be small rigid pieces such as microelectronic circuitry or much larger rigid items such as architectural glass. If the substrate is flexible, roll-to-roll processing is often used. Equipment is designed to handle the substrate in a manner that will promote the achievement of coating uniformity.

30.5 Properties of Sputtered Thin Film Coatings

The electrical, optical, and other properties of thin films often vary from the properties measured in bulk materials. Conditions present at the substrate during deposition can have a significant influence on these properties. When a sputtered atom condenses on a substrate, it transforms its kinetic energy to the surface lattice. The resulting loosely bonded atom has mobility on the surface and will migrate over the surface, interacting with other adsorbed atoms until it finds a permanent low energy site, or is desorbed. As the film thickness builds, atoms within the lattice move to more stable positions by bulk diffusion.

For many metals, the mobility of surface and bulk atoms is related to the ratio of substrate temperature (T) and the melting point of the metal (T_m). At low T/T_m values, surface and bulk diffusion play only a small role because atoms have insufficient energy to move from their initial position. In films deposited under these conditions (Figure 30.8), the internal crystal structure is poorly defined and has many defects; voids are also present due to shading effects. Conditions tending to produce lower T/T_m are higher melting temperature target materials (e.g., refractory metals), substrate cooling, higher working gas pressures (which “thermalize” or reduce sputtered atom energies), and reactive gases adsorbed on the surface. Higher T/T_m values result in more surface and bulk diffusion in the growing film, producing denser columnar grains with fewer defects and defined boundaries.

In addition to substrate heating, T can effectively be raised by bombarding the substrate with ions or electrons during deposition. In a diode system, the substrate is often in the plasma, resulting in film heating due to high energy electron impact. A bias voltage can also be applied to the substrate to accelerate incoming ions, increasing the kinetic energy transferred to the surface. When depositing alloys or compounds, higher T values may decrease the sticking coefficient of one component, changing the overall film composition. An important point to remember is that the kinetic energy of sputtered atoms typically is 10 times that of evaporated species. This factor plays a significant role in determining the difference in properties between sputtered and evaporated films.

Most sputtered thin films are in a state of compressive or tensile stress. The stress is due to the mismatch in thermal coefficients of expansion between the substrate and the thin film and to internal stresses built up within the film as a result of imperfections in the crystal lattice. In higher T_m materials, deposited at low T/T_m , internal stresses usually dominate and may reach the yield strength of the film, resulting in fracture. Both magnitude and type of internal stress have been found to be influenced by working gas pressure. Thermal stress usually predominates in higher T/T_m coatings.

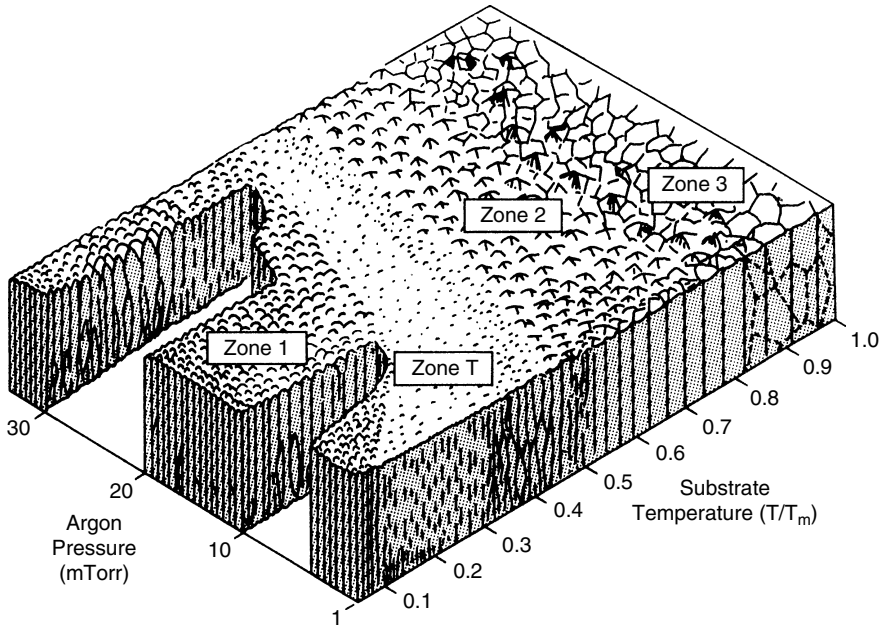


FIGURE 30.8 Schematic representation of the relationship between substrate temperature and argon pressure on the structure of metal coatings deposited by sputtering using a cylindrical magnetron source. T is the substrate temperatures and T_m is the melting point of the coating material in absolute degrees. (From J. A. Thornton, in *Deposition Technologies for Films and Coatings*, R. F. Bunshah, Ed. Park Ridge, NJ: Noyes Publications, 1982, p. 214.)

30.6 Thin Film Materials

Most metals have been deposited by sputtering; some of the more commonly used metals are aluminum, chromium, copper, gold, molybdenum, nickel, platinum, palladium, silver, tantalum, titanium, tungsten, vanadium, and zirconium. This group of metals represents an extremely broad range of electrical, magnetic, mechanical, optical, and other physical properties. If a single metal does not provide the necessary properties, alloys such as stainless steel, nichrome, and cobalt chrome may also be sputtered. The different elements comprising an alloy may have widely ranging sputter rates, but because of concentration at the target surface of the slower sputtering species, alloys can generally be sputter deposited with the same composition as the target. Semiconductors such as silicon and carbon can also be sputtered, but if conductivity of the target is too low, rf power may be necessary. Oxides, nitrides, carbides, sulfides, and other compounds of the metals, alloys, and semiconductors listed above may be made via reactive sputtering with added oxygen, nitrogen or ammonia, methane or other gaseous hydrocarbons, and hydrogen sulfide, respectively.

30.7 Applications for Sputtered Thin Films

Sputtered coatings are used for a wide variety of applications, some of which are listed below, according to the function performed by the thin film.

30.7.1 Electrical

Metals and alloys are used as conductors, contacts, and resistors, and in other components such as capacitors. Transparent conductors such as indium tin oxide and thin metals serve as electrodes for LCDs, touch panels, other display devices, and solar cells. Thin films are also extensively used in microelectronic devices.

30.7.2 Magnetic

Some high-performance magnetic data storage media are deposited via sputtering. Cobalt alloys such as cobalt–chromium and, to a lesser extent, nickel, iron, and samarium alloys are typically used.

30.7.3 Optical

Thin metal and dielectric coatings are used to construct mirrors, antireflection coatings, light valves, laser optics, and lens coatings, and to provide architectural energy control and optical data storage.

30.7.4 Mechanical

Hard coatings such as titanium carbide, nitride, and carbon produce wear-resistant coatings for cutting tools. Molybdenum sulfide serves as a solid lubricant.

30.7.5 Chemical

Thin film coatings can be used to provide high-temperature environmental corrosion resistance for aerospace and engine parts, catalyst surfaces, gas barrier layers, and lightweight battery components.

30.7.6 Decorative

Titanium nitride is deposited on watch bands and jewelry as a hard gold-colored coating. Metals are deposited for weight reduction in automotive and decorative graphics applications.

30.8 Additional Resources

The following professional societies include sections dealing with sputtered coatings: American Vacuum Society (offers short courses in sputtering and coatings), Society of Vacuum Coaters, Electrochemical Society, and Materials Research Society. Journals that cover developments in sputtered coatings include *Journal of Vacuum Science and Technology*, *Thin Solid Films*, *Journal of Applied Physics*, *Vacuum*, *Progress in Surface Science*, and the *Journal of the Electrochemical Society*.

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